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Procedia Engineering 44 (2012) 335 – 337

Procedia Engineering

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Euromembrane Conference 2012

[OB57]

Creating the new nanosize membrane reactors with accumulated hydrogen and uncatalytic hydrogenation of decene-1 using this hydrogen

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Introduction

Now, much attention is paid to the synthesis and investigations of materials composed of nanosized particles. Among these works, studies of carbon nanostructures (nanocrystallites, nanotubes, nanofibers, graphenes, etc.), which have extraordinary adsorption and electron emission properties, hold a special place. Investigation of heterogeneous catalytic reactions employing porous membranes has drawn a great amount of scientific attention recently. Development of the new generation nano-sized membrane reactors based on original carbon nanostructure are studied in this work. In such reactors hydrogenation reactions will be performed for the first time in the pores of ceramic membranes actively employing hydrogen which is preliminarily adsorbed in mono- and multilayered oriented carbon nanotubes with graphene walls (OCNTG) formed on the inner surface of pores.

Methods

Ultrafiltration composite membranes “TRUMEN” (TiO_2+MgO, and TiO_2+Cr_2O_3 on porous steel) were used in this work. The depth of the selective layer was ~ 20 mkm. Investigation of their porous structure using dynamic desorption porometry (DDP) showed that $D_{average}$ was 90, and 50 nm correspondingly; porosity was ~ 25-35%; surface area of pores was ~ 1.7 – 2.2 m^2.

Forming of OCNTG was performed at 800^{0}C in a set-up with quartz reactor (D_{inner} = 54 mm, L = 990 mm) and electric oven using a supply line of methane (~ 99% pure) as a pyrolysis agent.

Scanning electron microscope (SEM) investigation of chips of membranes was performed with the field emissive raster electron microscope JSM-6700F with add-on for energy-dispersive spectrometry (EDS) JED-2300F (JEOL, Japan). Analysis was performed with accelerating voltage of 15 kV, emission current of 10 mkA, primary electron bunch current of 5 nA and process distance of 8 mm.

Add-on JED-2300F was used for qualitative and quantitative analysis using EDS technique. In the investigation quantitative analysis with reference spectra of elements was used (function “differential filter + least-squares method + ZAF method”).

X-ray photoelectron spectroscopy (XPS) investigation was performed on the spectrometer PHI 5500 ESCA (Perkin Elmer) using Mg Kα radiation (hv = 1253.6 eV) with 300 W/ 14 kV power. Pressure of the residual gases in the measuring camera was 8-9x10^{-10} Tore. Fine spectrums were got with analyzer transmission energy of 11.75 eV and frequency of data acquisition of 0.1 eV/step. Correction of charging effects was performed by means of calibrating of binding energies scale relative to carbon $C1_s$ – 285.0 eV.

Amount of hydrogen adsorbed in OCNTG was determined using gravimetric method with the accuracy down to the hundredth parts of a milligram. The initial pressure of hydrogen at saturation was 10-13 MPa.

Temperature of H_2 desorption was determined by thermogravimetric analysis using SETSYS EVOLUTION 16/18 (Setaram) combined with mass spectrometer OmniStar GSD 301 (Pfeiffer). Samples of membranes ~ 0.5 g with OCNTG synthesized in their pores containing accumulated hydrogen were hung up on a quartz rod in the center of the heating zone. The cell was filled with He before analysis. Delay time of the mass-spectrometric analysis was ~ 8 sec. Ion current values at *m/e* = 2, 18, 28, 32, 44 were fixed on line.

The electric surface properties of membranes were investigated using the flow potential method with chlorine-silver (Ag-AgCl) electrodes. In this investigation, the potential drop ΔE was studied as the function of pressure drop ΔP in the membrane when 0.01 M solution of KCl was put

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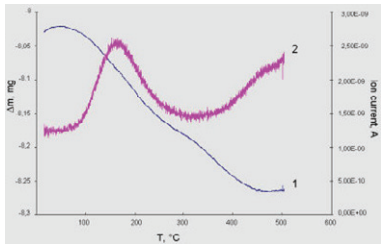
doi:10.1016/j.proeng.2012.08.407



through the membrane. The flow potential (ΔE/ΔP) was used to determine the value of *ξ*-potential using Smoluhovski equation; this latter value was used in Gui equation for determination of charge density on the porous surface. The sign of the surface charge was determined using the slope ratio of ΔE/ΔP.

Chromatograph analyzing of decene-1 and its products carrying out with using quartz column 200×0,30 mm with liquid phase of FFAP (thickness – 0,32 mkm). Concentration of substrates was estimated with using absolute preliminary calibration on based data obtained from 5 measurements.

Results

The new technique of synthesis of new carbon nanostructires is proposed: the oriented carbon nanotubes with graphene walls (OCNTG). To synthesize these structures the consistent covering of surface of pores of ultrafiltration inorganic membranes ($D_{av.}$= 50 and 90 nm) with monolayers of graphenes was held. These monolayers were formed during pyrolysis of the definite quantity of methane.

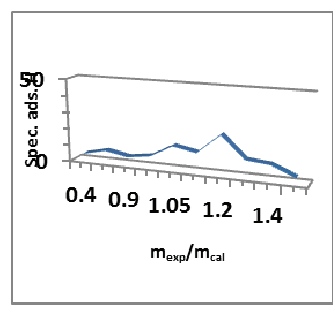
Formation of OGCNTs in the membrane pores was carried out under Knudsen diffusion conditions (deposition over the whole pore depth). The depth of covering with monolayer was controlled with SEM.

The samples of membranes modified by mono- and polylayers of OCNTG were preparing and saturated by hydrogen at 9,0 - 12,0 MPa. Investigation of regularities of adsorption, storage and desorption of hydrogen in OCNTG were carry out. It was shown that quantity of the adsorbed hydrogen reached 14,0% from mass of OCNTG. Adsorption of hydrogen in OCNTG was identified for the first time using thermogravimetric analysis (TGA) coupled with mass-spectrometric analysis, and it was found that its desorption at atmospheric pressure occurs at temperature of ~ 175^{0}C. On the left figure represent change of mass (1) and ion current (2) at *m/e* =2.

On the right figure a dependence of hydrogen specific adsorption (mg/monolayer OCNTG) on the relation of experimentally supported hydrogen mass at OCNTG formation to mass, which was calculated by the equation (proposed by one of the authors) is shown. The resulted curve has maximum at m_{exp}/m_{cal} = 1,2. Probably, in this case we have the most ideal stricture of OCNTG with minimum of defects. Consequently, the relation m_{exp}/m_{cal} = 1,2 (defined as ψ) can be considered as a numerical factor, which is characterized an ability of OCNTG to adsorb and storage of hydrogen if the relation 0,4-0,6 < Ψ < 1,5-1,7 is realized. On the other hand this curve demonstrate how hydrogen adsorption ability change in row of carbon nanostructures: graphenes (Ψ < 0,4) - no hydrogen adsorption → OCNTG (0,4-0,6 < Ψ < 1,5-1,7) – adsorption take place → pyrocarbon nanocrystallites (1,7 < Ψ) - no hydrogen adsorption.

It was elaborated the methodic of hydrogenation reaction carrying out inner membrane pores modified by OCNTG contained accumulated hydrogen. For this porpoise the design drawings and catalytic cell were created. The catalytic cell construction permits to fasten membrane between two flanges equipped by sealing disk. By way inert gas passing the products reaction can be desorbed from carbon covering and accumulated in the receiver cooling by liquid nitrogen. The samples of membranes with D_{pores} - 50 and 90 nm modified by three layers of OCNTG were preparing and saturated by hydrogen at 9,0 - 12,0 MPa. After that membrane systems were filling up by decene-1. Reaction of decene-1 hydrogenation carrying out at temperature 250-350^{0}C, pressure (N_2)- 2,0-6,0 mPa and time residence - 30-240 min without catalyst loading. It was estimated that concentration of decane in initial decene-1 - 0,46 ±0,03%. Uncatalytic hydrogenation reaction was carry out and the quantity of decane increases up to 0,64± 0,05% - 1,5 ± 0,05%.

The new effect of hydrogen variation of performance (HVP) was found; this effect consists in that fact that hydrogen adsorbed in OCNTG influences in transport properties of membranes decreasing their performance on liquids in 4-26 times which fact is the indirect confirmation of its high activity which rides probably on dissociative mechanism of hydrogen adsorption.



Discussion

Very important for our investigation is the question about the mechanism and the energy of hydrogen adsorption in

OCNTG; the detailed report on this problem will be presented in the subsequent publications. However, we'd like to note that the temperature of H_2 desorption (170 – 180 ^{0}C) shows that energy of its binding with OCNTG is significantly higher than the energy of the hydrogen bond. It is known [1] that the energy of the hydrogen bond for water molecules which form 4-molecule associates at 0^{0}C it rather high and is equal to 25 kJ/mol. However, at the boiling point and under atmospheric pressure water contains less than 1% of dimers [2], i.e. hydrogen bonds are destroyed almost entirely.

At the same time, hydrogen is stored in OCNTG up to significantly higher temperatures, 170 – 180 ^{0}C. In the case of dissociative adsorption of H_2 in OCNTG the forming bonds are weaker than typical chemical C-H bonds; in the case of non-dissociative adsorption the interaction under review is much more stronger than physical sorption (Van der Waals forces, energy of desorption is of the same order as the enthalpy of evaporation of liquid hydrogen, i.e. ~ 0.9 kJ/mol [3-4]). In the case of the dissociative adsorption, the mechanism of hydrogen spillover [5] is possible while in the second case, the structurally-adsorptive mechanism is possible.

Thus, new carbon nanostructures were synthesized, namely, oriented single- and multiwall carbon nanotubes with walls formed of graphenes. They turned out to be able to adsorb and store molecular hydrogen and their adsorption capacity is in line or larger than similar value of traditional carbon nanotubes.

Results on adsorption and storage of H_2 in OCNTG formed in pores let one to consider membrane as the integrity of ~ 25 10^{10} of nano-size reactors in which ~ 4,84 10^{-4} mol of hydrogen is accumulated. It is shown for the first time that desorption of hydrogen from OCNTG occurs at 170-180^{0}C which is typical for many hydrogenation reactions. This result firstly demonstrated decene-1 hydrogenation reaction flowing without catalyst with using hydrogen has been accumulated and storage in carbon nanostructires. Besides that obtain data confirm, under certain conditions, the mechanism of hydrogen spillover. Obtained results completely confirm conception suggested by authors relates to creation of nano size membrane reactors posses ability hydrogen accumulating.

Effect of hydrogen variation of performance (HVP) for membranes with OCNTG synthesized in pores with hydrogen accumulated in that OCNTG which was found for the first time can be considered as the indirect confirmation of high activity of H_2 adsorbed in two-dimensional structure. The registered increase of surface charge and of ξ-potential is connected probably with dissociative mechanism of hydrogen adsorption.

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Keywords: carbon nanotubes, graphenes, membrane reactors with accumulated hydrogen, uncatalytic hydrogenation using accumulated hydrogen